

Mechanisms for higher T_C in copper oxide superconductors; Ideas from band calculations.

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Band calculations for the hole doped La_2CuO_4 system show that artificial periodicities of Ba dopants can give the material different properties than from a uniform distribution of dopants. A periodicity within the planes make static pseudogaps which could be tuned to raise the density-of-states (DOS) at E_F and the superconducting T_C . A periodic doping dependence perpendicular to the CuO planes can increase the matrix element for spin fluctuations.

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Band calculations for high- T_C copper oxide systems have shown that phonon distortions within the CuO-planes are favorable for anti-ferromagnetic (AFM) spin fluctuations [1]. Such type of spin-phonon coupling (SPC) can be responsible for (dynamic) stripes and pseudogaps, since a periodic potential $V_q \exp(-i\vec{q} \cdot \vec{x})$ leads to a gap $2V_q$ at the zone boundary [2]. The qualitative results of ab-initio calculations and free-electron like parametrization are able to describe several typical and unconventional features of the high- T_C 's [3]. For instance, the pseudogap is according to SPC more developed at low doping leading to a low density-of-states (DOS) at the Fermi energy (E_F) and is therefore in competition with superconductivity [3]. The role of stripe order and the importance of non-uniform doping for the properties of the cuprates has been discussed theoretically and experimentally [4, 5]. There is no consensus about the mechanism of superconducting pairing in the high- T_C copper oxides, but a high DOS at E_F , $N(E_F)$, is good for superconductivity in theories based on electron-phonon coupling, λ_{ep} , as well as on coupling due to spin fluctuations, λ_{sf} . Here are proposed different ways of increasing $N(E_F)$ and/or the exchange interaction for AFM spin fluctuations through periodic doping distributions. This is done through band calculations, using the Linear Muffin-Tin Orbital (LMTO) method in the local spin-density approximation [3], for large unit cells with superstructures of La/Ba substitutions in $\text{La}_{(2-h)}\text{Ba}_h\text{CuO}_4$ (LBCO). One calculation for a small cell is based on the virtual crystal approximation (VCA), where the nuclear and electronic La-charges (57.0) are reduced to (57- $h/2$) to account for a perfectly delocalized doping, h , in holes per Cu.

Two types of superstructures are considered. The first is for extensions of the unit cell parallel to the CuO planes along the \vec{x} -axis. The objective is to find a mechanism to oppose the drop in $N(E_F)$ caused by the pseudogap in underdoped LBCO, or even to increase $N(E_F)$ when there is no pseudogap in overdoped cases. The idea is to chose the strength (V^*) and wavelength (Λ^*) of a static potential modulation so that one of the resulting DOS peaks (above or below the induced gap) will be at E_F .

A simple doubling of one La_2CuO_4 cell in the x-y-plane makes up the basic AFM cell with opposite spin on the

two Cu sites. Large cells containing totally 56 or 112 sites are made by putting together four or eight of such AFM cells along \vec{x} (with lengths 4 or 8 times the lattice constant a_0), where Ba/La substitutions create the potential modulations along the supercell. Three calculations are made for cells of length $8a_0$. One is where the 4 La surrounding the two Cu within the first row (along \vec{y}) are replaced with Ba. The fraction of sites occupied by Ba, f , is 1 within this row, while no other Ba/La substitution is made in the other 7 rows further down along \vec{x} . This makes the effective doping h equal to 0.25 holes/Cu, and the "periodicity" (Λ^*) of the doping is $8a_0$. A second case with $h=0.125$, is considered in the same cell except that only half of the La-sites are exchanged with Ba in zigzag-like pattern along \vec{y} ($f = \frac{1}{2}$). The same two sets of configurations are also made for a half as long cell along \vec{x} ("periodicity" $4a_0$), with doping $h=0.5$ and 0.25 respectively. The third case with 112 sites is with two adjacent rows of complete La/Ba exchange, i.e. for $h = 0.5$ and $f = 2$.

The calculated variation of charge, ΔQ , and potential shift, V^* , on Cu are shown in Table I. The charges on Cu near Ba-sites decrease because of an upward shift of the potential, and the widths of the Cu-d band become

TABLE I: Ab-initio LMTO results for periodic La/Ba substitution along \vec{x} . The doping h is in holes per Cu, and f is the fraction of Ba occupation within the doped rows ($f=2$ is for two adjacent rows of complete La/Ba exchange). The periodicity Λ^* is the distance (in a_0 -units) between the doped rows. The $N(E_F)$ (in states/Ry/Cu) is obtained from a rigid-band shift (to account for the doping, h) on the DOS of undoped La_2CuO_4 , shown in Fig. 1. The largest charges (Q , electrons per Cu) and attractive potential shifts on Cu (V^* , mRy) are in regions far from the Ba-dopants.

h	f	Λ^*	$N(E_F)$	Q_{Cu}	V^*
0.125	$\frac{1}{2}$	$8a_0$	25.0	$10.36 \pm .17$	6.6
0.250	1	$8a_0$	16.5	$10.33 \pm .18$	11
0.250	$\frac{1}{2}$	$4a_0$	16.5	$10.36 \pm .11$	6.4
0.500	1	$4a_0$	10.0	$10.31 \pm .15$	14.5
0.500	2	$8a_0$	10.0	$10.31 \pm .23$	23.3

narrower (~ 10 -20 percent). It is quite natural that V^* is large for large f , since the influence on Cu will be larger with many Ba nearby. The second trend, larger V^* for short periodicities, is connected with large doping, lower $N(E_F)$ and less effective screening. The V^* are of similar size (5-10 mRy) as V_q from typical phonon distortions [6].

The wave length Λ (in units of a_0) of the phonon wave in SPC is proportional to the inverse doping, $\Lambda = 1/h$ (the wave length of the spin wave is twice as long). This is for not too large doping, and E_F is at the pseudogap [3]. The doping can be chosen so that $\Lambda^* \approx \Lambda$. But this is not the the main interest here, because even if spin fluctuations are responsible for the pseudogap in SPC, it is not obvious that a static gap should promote spin fluctuations. Instead, the goal is to create humps in the DOS near E_F . In order to have a large V^* , and large humps around a deep gap, it is probably good to have a sizeable La/Ba-exchange within the given row and a clear separation between the rows, if the number of dopants allow for that.

The imposed spacing Λ^* between Ba-rich rows can be related to a fictive doping h^* , $\Lambda^* = 1/(h + h^*)$, where h^* is number of states between E_F and the energy (E^*) at the static gap, with the requirement that $(E_F - E^*) \approx V^*$. From an effective DOS between E^* and E_F , \tilde{N} , this defines a positive $h^* = \tilde{N}V^*$ (holes) for a positive V^* , with E_F at the DOS-hump above the static gap. This will be best at underdoping, while the use of a hump below the gap (negative V^* and h^*) is appropriate in overdoped cases. The fraction $f = h\Lambda^*$, is not a free parameter, but it has to fit with the true doping. A very small f is not appealing, since the dopants will be diluted in many closely spaced rows with very weak V^* . That would look more like a random distribution of the dopants. Stronger modulations from well structured dopings are preferred.

Results for different dopings, shown in Table II, are based on interpolated values from Table I. For example, if the doping is 0.05 it is best to replace 1/3 of La with Ba within every 7th (6.7) row for a good increase of the DOS at E_F . Higher doping $h = 0.15$ would require 1/2 (0.54) La-Ba replacements within every 4th (3.6) row, and so on. "New" gaps would appear 4-6 mRy below E_F in these cases. A case with extreme overdoping, $h = 0.48$, can hardly support strong SPC because the wave would be too short. But if it should be made it would require complete La/Ba exchange within 2 rows ($f = 2$) separated by ~ 2 rows of pure La ($\Lambda^* \approx 4-5$) to increase the DOS at E_F . The static gap would be ~ 20 mRy above E_F . The gap is wide because V^* is large when all dopants are concentrated within few layers, and it forces the modulation to be short. The last line in Table II, is a suggestion for a sinusoidal profile of La/Ba-exchange along the cell ($f = 3.3$ but the doping is spread over more than 3 rows), in order to diminish the effective V^* and to have a more reasonable Λ^* .

It is difficult to quote precise enhancements of the DOS at E_F for these periodic dopings. But in previous calculations with comparable amplitudes of V_q for phonon dis-

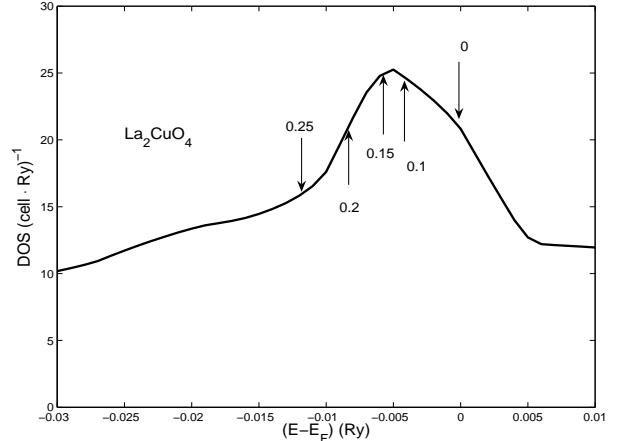


FIG. 1: The DOS near E_F for La_2CuO_4 . The arrows with the numbers indicate the rigid-band position of E_F at the respective doping (holes/Cu). For 0.5 holes E_F would be at -0.030 Ry.

tortions, the enhancements can easily be 30-50 percent within peak widths of the order 3 mRy [3].

The second type of superstructure is for modulations perpendicular to the CuO-planes along the \vec{z} -axis. Such modulations should be simpler to make than in-plane modulations. For example, films with doped and undoped layers have been made with higher T_C than for optimally doped bulk [5].

Spin-polarized calculations, with applied magnetic fields of $\pm 5\text{mRy}$ on each Cu, are made for 4 basic AFM unit cells above each other, with a total of 56 sites (4 CuO layers) in the cell. Two dopings, $h=0.125$ and $h=0.25$, are considered by replacing 1 or 2 La with Ba. The replacement with 2 Ba surrounding a Cu layer can be made in three different ways. One possibility ("zigzag") is when one Ba is put above one of the two Cu in the first layer, while the other Ba is put below the second Cu in the same layer. Another ("column") is when only the La close to the first Cu are replaced with Ba, and the third possibility ("plane") is to fill one whole La layer with Ba. The average h is 0.25, but the structures can be viewed as 3

TABLE II: The required spacing (Λ^* in units of a_0) between Ba-rich rows for optimal enhancement of the DOS at E_F for some dopings. The unenhanced $N(E_F)$ is in states/Ry/Cu, and V^* in mRy.

h	f	$N(E_F)$	h^*	V^*	Λ^*
0.05	0.33	22	0.10	4	6.7
0.10	0.42	23	0.14	6	4.2
0.15	0.54	22	0.13	6	3.6
0.20	0.58	21	0.15	7	2.9
0.48	2	12	-0.24	-20	4.2
0.25	3.3	16	-0.18	-11	13.5

undoped layers sandwiched between single layers of heavily doped LBCO. The DOS near E_F show no clear gap structures, but there are variations of the local exchange enhancements.

Table III displays the results. The charge transferred from Cu atoms near the Ba dopant is important, as shown by the lowest charges in Table III, and the largest charges on Cu within La rich regions can even surpass the Cu charge for the undoped case. The first four lines, for perfectly delocalized doping in the VCA, show the general trend of weaker AFM spin waves at large doping (Ferromagnetism, FM, appears in the VCA for much higher h [7]). The moment per Cu is highest ($\sim 0.14\mu_B$) in the undoped case, and it goes down with doping to reach ~ 0.06 for $h=0.375$ holes per Cu. The calculations using a supercell distribution of 1 or 2 Ba substitutions show that larger moments (averaged and even more locally) are obtained if the dopants are distributed within few layers only. For instance, for 2 Ba in one plane ($h=0.25$) the average moment per Cu is 40 percent larger than the moments in VCA at the same doping. The largest moments, 2.5 times larger than the VCA moments, are found within the Cu layer next to the Ba layer. On the most distant Cu layers the moment is near 0.07, as in VCA. By having another distribution of the two Ba near a Cu layer ("column" and "zigzag") one obtains somewhat weaker spin waves, but still considerably stronger than seen with VCA.

The conclusion from the result with one Ba is partly different. The average moment is smaller than in VCA (0.109), but with large local variations. The largest moments (~ 0.125) are found in the next nearest Cu layer. Moreover, this case and the 2 Ba "column" case have another complication in common; The AFM waves on Cu are perturbed locally near the Ba dopants so that the majority moment is considerably larger than the minority moment in the same layer, as if FM would profit from AFM. Weak FM can also appear around clusters of Ba in larger supercells [7]. In contrast, spin-polarized calculations for AFM waves in a cell with modulated doping along \vec{z} ($f=1$, $\Lambda^* = 8a_0$) show no sign of FM perturbations.

Thus, the result for modulated doping along \vec{z} shows that enforcement of spin waves can be achieved, more so locally near the doped layers than for the average over the whole cell. This implies a larger λ_{sf} , since $\lambda_{sf} \sim NI_m^2$,

where the matrix element for spin fluctuations, I_m , is proportional to m [2], and a possibility for a higher superconducting T_C . It can be noted that calculations show also an enhancement of spin waves at the surface of La_2CuO_4 [8]. This is in line with the observation of enhanced T_C at the strained interface between undoped LBCO and SrTiO_3 [9], even though deformation and oxygen migration are important factors. Stronger effects from combinations of parallel and perpendicular modulations seem plausible.

In conclusion, modulation of doped layers can be a possibility to enhance T_C through AFM spin fluctuations, but competition with FM might be destructive for some configurations. Modulations along the layers seem more promising, since it can bring more states close to E_F . It will be an experimental challenge to find a technique for making such modulations. Distortion is not considered in these calculations, but periodic distortions and strain near interfaces would be another possibility for creating potential modulations along the planes.

TABLE III: VCA and LMTO supercell results for perpendicular modulations at different dopings. Smallest and largest charges (q_{min} and q_{max}), average and maximum of the absolute values of magnetic moments (\bar{m} and m_{max}) on Cu for different doping (h in units of holes per Cu) for different configurations of LBCO. All Cu-sites are equal in the results based on the VCA. Three results for different positions of the two La-Ba substitutions are listed ("plane", "column" and "zigzag", see the text). The basic AFM spin configuration is imposed in all cases through application of magnetic fields of ± 5 mRy on the Cu. The last column shows that a FM moment (m_{FM} , μ_B per cell) remain in two cases, which indicates that Ba impurities perturb the imposed AFM state.

h	q_{min}	q_{max}	$ \bar{m} $	$ m_{max} $	m_{FM}
0.000 (VCA)	10.393	10.393	0.138	0.138	-
0.125 (VCA)	10.369	10.369	0.109	0.109	-
0.250 (VCA)	10.345	10.345	0.070	0.070	-
0.375 (VCA)	10.322	10.322	0.063	0.063	-
0.125	10.272	10.455	0.089	0.125	0.097
0.250 "plane"	10.207	10.463	0.098	0.173	0.000
0.250 "col."	10.183	10.489	0.087	0.132	0.213
0.250 "zig."	10.183	10.490	0.085	0.130	0.000

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